EXAFS spectra above Pb and Pt *K* edges observed at low temperature

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X-ray absorption spectra near *K* edges of Pb (88.0keV) and Pt (78.4keV) for the foils were measured in transmission mode at SPring-8. We succeeded for the first time in observing the EXAFS oscillation of the Pb foil at 12K, although it was failed at room temperature in a previous experiment. The amplitude of the EXAFS oscillation of the Pt foil at 12K considerably increased in comparison with that at room temperature, indicating that the amplitude is very sensitive to the Debye-Waller factor at high-*k* values.

keywords: XAFS, high energy, Pb *K* edge, Pt *K* edge, Debye-Waller factor.

1. Introduction

The EXAFS (Extended X-ray Absorption Fine Structure) spectrum with *K* absorption edge is expected to improve the accuracy of local structure parameters for the elements such as lanthanoids, whose energy range just above the L_{III} edge is restricted owing to the following L_{II} edge. It is also well known that the finite lifetime of a core hole smears out the EXAFS oscillation, and that this effect becomes more serious for heavier elements (Stearns, 1984). The amplitude of the EXAFS oscillation is reduced especially in the range of low wavenumber *k* for the photoelectron by the smearing effect, and is also reduced for outer shells, namely, higher frequency component in *k* space. Moreover, it is rather difficult to extract an EXAFS signal at low-*k* values because of a broad edge depending on the finite lifetime of the core hole. The fitting calculation of EXAFS for heavy elements is generally carried out at higher-*k* values. The EXAFS oscillation can be observed in the high-energy region when it is measured carefully in the case of the heavy backscatter because the backscattering amplitude for the photoelectron is inherently large at high-*k* values. We can also expect the increase of the amplitude of an EXAFS oscillation at low temperature since it might be considerably affected by the Debye-Waller factor at high-*k* values.

The utility to *K* edge EXAFS measurement was shown by analyzing the EXAFS spectra for some *K* edges (Ce, Dy, Ta and Pt) in the previous work (Nishihata et al., 1998): local structure parameters were successfully evaluated from the EXAFS signal near the *K* edges as well as the L_{III} edges. Any EXAFS signal could not be observed above the Pb-*K* edge (88.0 keV) at room temperature (Nishihata et al., 1999). Here we report the first observation of the EXAFS spectrum above the Pb-*K* edge for a Pb foil at 12 K. We also show that the amplitude of the EXAFS

signal increased remarkably above the Pt-*K* edge (78.4 keV) at low temperature in comparison with that observed at room temperature.

2. Experimental and analysis

XAFS (X-ray Absorption Fine Structure) spectra near *K* edges of Pt and Pb for the foils were measured at bending-magnet
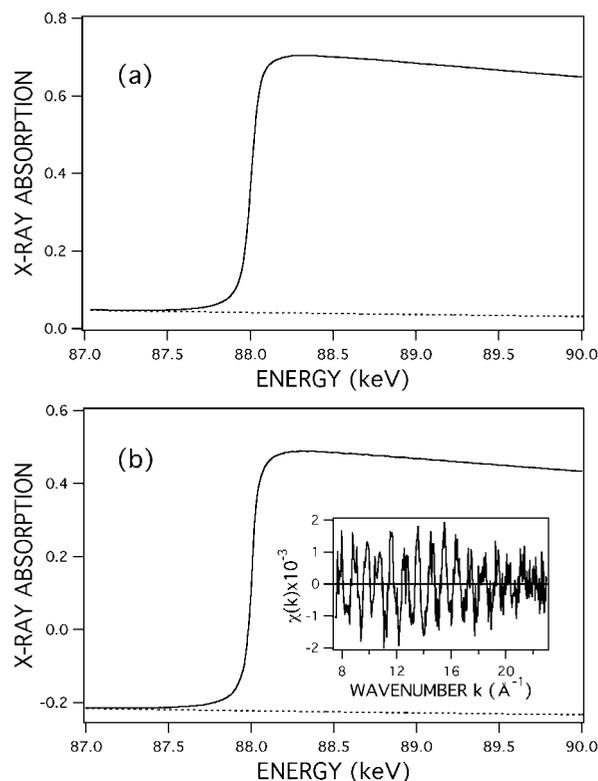
Figure 1
XAFS spectra for a Pb foil at (a) 299 K and (b) 12 K. The inset gives the EXAFS function χ(*k*).
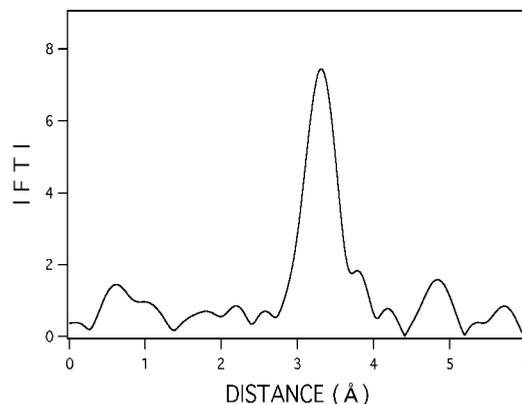
Figure 2
Magnitude of the Fourier transform of k^3-weighted EXAFS function χ(*k*) for the Pb foil at 12 K.

beamline BL01B1 at SPring-8. Measurements were carried out at 299 K and 12 K in transmission mode with Si (511) planes of a double crystal monochromator. The incident and transmitted x-ray intensities were monitored with a flowing Kr gas ionization chambers of 17 cm and 31 cm in length, respectively. Counting of higher-order harmonics was estimated to be less than 1 % by considering both of photon flux of the source and efficiency of the detector. Although the cross section of the Compton scattering increases in the high energy region, it is almost independent of energy within the energy range for a standard XAFS measurement. The energy resolution at the Pt and Pb K edges were estimated to be 7 and 8 eV, respectively, from the vertical size of the x-ray source (0.1mm) and the width of the vertical slit at 47 m from the source (0.2mm).

The EXAFS function $\chi(k)$ was extracted from the absorption spectrum following the standard procedure and was normalized using MacMaster coefficients. The programmes *XAFS93* and *MBF93* (Maeda, 1987) were employed for the data analysis to determine local structure parameters. The EXAFS formula is based on single-scattering theory and expressed by the cumulant expansion (Ishii, 1992):

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} \left| f_j(k, \pi) \right| \exp(-2\sigma_j^{(2)} k^2 + \tfrac{2}{3}\sigma_j^{(4)} k^4) \exp(-\frac{2R_j}{\lambda_j})$$

$$\times \sin\left[2kR_j - \frac{2k}{R_j}\left(1 + \frac{2R_j}{\lambda_j}\right)\sigma_j^{(2)} - \tfrac{4}{3}\sigma_j^{(3)} k^3 + \Psi_j(k) \right], \quad (1)$$

where N_j is the coordination number in the jth shell at distance R_j from the absorbing atom, $|f_j(k, \pi)|$ is the back-scattering amplitude of photoelectrons, and $\psi_j(k)$ is the total phase shift function (McKale et al., 1988). The quantities $\sigma_j^{(n)}$ are the nth cumulants. The mean free path λ_j of the photoelectron was taken to depend on the wavenumber k with the relationship $\lambda_j = k/\eta_j$. When we take a harmonic vibration model, the quantities $\sigma_j^{(3)}$ and $\sigma_j^{(4)}$ must be zero. A Fourier-filtered EXAFS function of the peak in real space was compared with a theoretical EXAFS function. In the parameter fitting, the theoretical EXAFS function was filtered in the same way as the observed one in order to eliminate truncation effects through the Fourier transformation.

3. Results and discussion

Figures 1 (a) and (b) show XAFS spectra near the Pb-K edge for a Pb foil at 299 K and 12 K, respectively. Any fluctuation of the XAFS spectrum was not observed above the Pb-K edge at room temperature, while it was observed at 12 K. The inset gives the extracted EXAFS function. Figure 2 shows the radial structure function around the Pb atom obtained by Fourier transform of k^3-weighted EXAFS function $\chi(k)$. Local structure parameters about the first nearest neighbour are given in Table 1. The interatomic distance is close to the value obtained by x-ray diffraction in literature. The value η is estimated to be larger than that of the Pt depending on shorter lifetime of the Pb-K hole. Unfortunately, the quality of the EXAFS signal is not enough to carry out the fitting for an anharmonic model.

Figures 3 (a) and (b) show XAFS spectra near the Pt-K edge for a Pt foil at 299 K and 12 K, respectively. A remarkable increase of the amplitude in the fluctuation of the XAFS spectrum was obsereved at 12 K. The insets give the EXAFS functions

which were extracted from the absorption spectra. The amplitude of the EXAFS function increases considerably especially at high-k values. Even high frequency component was seen clearly at k higer than 17 Å^{-1}. Figure 4 shows radial structure function around the Pt atom obtained by Fourier transform of k^3-weighted EXAFS function $\chi(k)$ for 299 K and 12 K. The fitting analysis was carried out concerning the
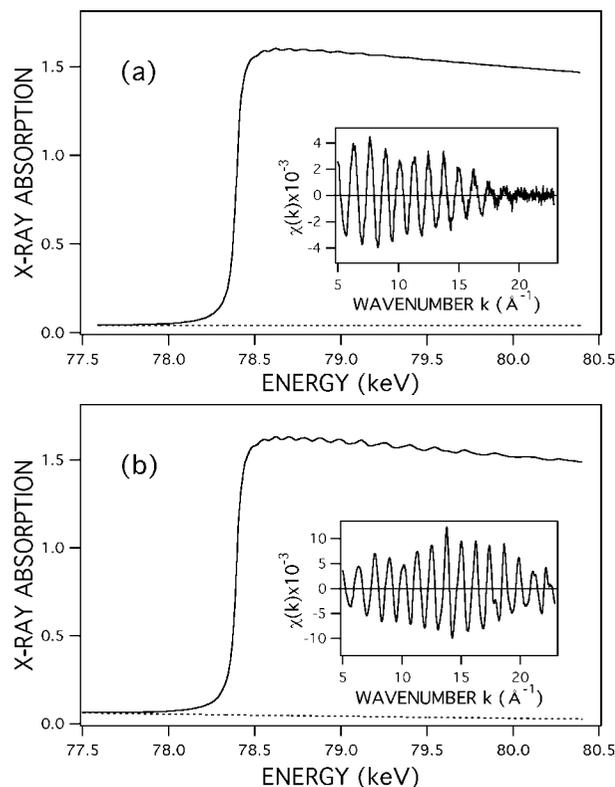
Figure 3
XAFS spectra for a Pt foil at (a) 299 K and (b) 12 K. The insets give the EXAFS function $\chi(k)$.
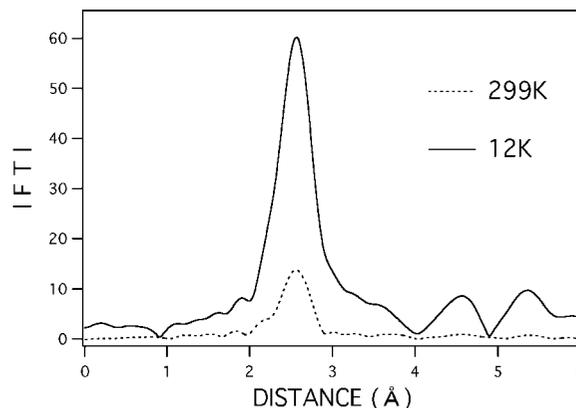
Figure 4
Magnitude of the Fourier transform of k^3-weighted EXAFS function $\chi(k)$ for the Pt foil at 299 K and 12 K.

data analysis

Table 1
Local structure parameters of Pb and Pt foils for the harmonic model. The coordination number was fixed at 12.

shell	T (K)	R (Å)	$\sigma^{(2)}$ (10^{-2} Å^2)	η (Å^{-2})
Pb-Pb	12	3.492(4)	0.34(2)	4.36(18)
Pt-Pt	299	2.768(2)	0.45(1)	4.08(10)
Pt-Pt	12	2.777(4)	0.14(1)	3.88(3)

Table 2
Local structure parameters and thermal expansion coefficient of Pt foil at 299 K and 12 K for the anharmonic model. The coordination number was fixed at 12.

T (K)	R (Å)	$\sigma^{(2)}$ (10^{-2} Å^2)	$\sigma^{(3)}$ (10^{-4} Å^3)	$\sigma^{(4)}$ (10^{-5} Å^4)	η (Å^{-2})	α (10^{-6} K^{-1})
299	2.786(3)	0.50(2)	0.8(2)	0.4(2)	3.92*	10(2)
12	2.772(3)	0.13(1)	-0.2(1)	0.0(1)	3.92(8)	0.0(1)

*The parameter η at 299 K was taken to be the same as that at 12 K.

peak of the first nearest neighbour. The results for a harmonic model are given in Table 1. Here the coordintion number was fixed to 12. The Debye-Waller factor $\sigma^{(2)}$ at 12 K is 1/3 of that at room temperature. The atomic distance between the central atom and the first nearest neighbour at room temperatrure is shorter than that at 12 K because an anharmonicity of atomic vibration is not ignored at room temperature. Local structure parameters for an anharmonic model are given in Table 2. The interatomic distance at room temperature is compensated and is in good agreement with 2.775 Å in literature within a deviation of about 0.01 Å. We can evaluate thermal expansion coefficient α using the relation derived by Frenkel & Rehr (1993):

$$\alpha = \frac{\sigma^{(3)}}{RT\sigma^{(2)}} \frac{3z(1+z)\ln(1/z)}{(1-z)(1+10z+z^2)}, \tag{2}$$

where $z = \exp(-\Theta_E/T)$, and Θ_E and T are the Einstein and absolute temperatures, respectively. Here the Einstein temperature was estimated to be 172 K using the Einstein model:

$$\sigma^{(2)}(T) = [\hbar^2/(\mu k_B \Theta_E)]\coth(\Theta_E/2T), \tag{3}$$

where μ is the reduced mass of the relevant atomic pair (Pt-Pt), $\hbar$ and k_B are Planck's and Boltzmann's constants, respectively. The thermal expansion coefficient α at room temperature was good agreement with 9.0 x 10^{-6} K^{-1} in literature, while the α was estimated to be zero at 12 K.

4. Conclusion

XAFS spectra near the Pb-K edge for a Pb foil were measured at 299 K and 12 K. Any EXAFS signal was not observed at 299 K, while an EXAFS signal was observed for the first time at 12 K and was analyzed for a harmonic model. XAFS spectra near the Pt-K edge for a Pt foil were measured at 299 K and 12 K. The remarkable increase of the amplitude of the EXAFS oscillation was observed at 12 K. The qualitative EXAFS signal on Pt was obtained enough for an anharmonic analysis. The remarkable increase of the EXAFS signal at low temperature indicates that EXAFS signal at high-k values in the high-energy region is very sensitive to temperatures. This property seems to be useful for the study concerning lattice vibration or interatomic potential.

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